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Extended Summaries Pesticides in Food and Drink

The following are extended summaries based on papers presented at the 1st European Pesticide Residue Workshop, 'Pesticides in Food and Drink', held at Alkmaar, The Netherlands on 10–12 June, 1996. They are entirely the responsibility of the authors and do not necessarily reflect the views of the Editorial Board of Pesticide Science.

An Inter-laboratory Comparison Study of Two CEN Multi-residue Methods for Use in the Enforcement of Maximum Residue Levels for Pesticides in Fruit, Vegetables and Grain within the European Union

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Introduction

The Standards, Measurement and Testing (S, M & T) Programme was established by the European Commission (EC) to fund work on expanding and improving the quality of science and technology within the European Union (EU). Many projects are aimed at the attainment of mutual recognition of analytical data between member countries.

Complementary to the S, M & T Programme is the work of the Comité Européen de Normalisation (CEN). A Technical Committee (TC) 275 of CEN was established in 1991 with the remit to produce harmonised European Standards containing horizontal (equivalent) methods for food analyses. Only methods which were in widespread use throughout the Community and which had validation data demonstrating a satisfactory performance were selected.

Working Group 4 of TC 275 (Methods of Analysis for Pesticide Residues in Non-Fatty Foods) has recently produced a draft Standard which includes two multi-residue methods (P[1] & R[2]), both using gel permeation chromatography as a clean-up technique.[1–3] Although both procedures have recovery data to support them, neither has been fully validated in terms of a comprehensive inter-laboratory comparison or collaborative study.

The main difference between the methods is that Method P employs acetone as the extraction solvent, whereas Method R utilises ethyl acetate. An EC-funded project to compare the performances of these two CEN methods was initiated earlier this year, the main aim of which was to test the relative extraction efficiencies of the two methods by using a number of pesticides which exhibit a diverse range of physicochemical characteristics. The methods will be tested not only with 'laboratory spiked' samples but also with samples from crops which have been treated with pesticides under normal agricultural practice to induce 'incurred' residues.

Choice of the pesticide/commodity combinations to be studied

It would be impossible to study all the possible pesticide/commodity combinations as these would run into tens of thousands, hence the selection of pesticides and commodities must be as diverse as possible in order to represent the main classes of pesticides and the major types of non-fatty foods. (See Table 1).

The choice of pesticides was made by considering the following criteria:

(i) the pesticides should be known to produce residues which have, or may form, the basis of trading problems;
(ii) they should include typical examples from the major chemical classes of pesticides, i.e.

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TABLE 1
Pesticide Commodity Combinations Chosen for Study

Commodity	*Pesticides*
Strawberries	bupirimate, chlorpyrifos, dichlofluanid, iprodione
Spinach	bifenthrin, dimethoate, omethoate, metalaxyl, permethrin
Carrots	chlorfenvinphos, cypermethrin, dimethoate, omethoate, metalaxyl, triazophos
Tomatoes	bupirimate, chlorothalonil, α-endosulfan, β-endosulfan, endosulfan sulfate, tetradifon, tolylfluanid
Apples	bromopropylate, captan, fenoxycarb, phosalone, thiabendazole
Wheat	chloropyrifos-methyl, deltamethrin, lindane, permethrin, pirimiphos-methyl

organophosphorus, pyrethroid, carbamate, organochlorine etc.;
(iii) they must be widely used throughout Europe;
(iv) they should exhibit a range of physicochemical properties;
(v) crop treatments must be agronomically realistic, i.e. the pesticides must be selected from those approved for use on that particular crop within the European Union;
(vi) they must be amenable to gas chromatographic analysis to limit the amount of work for participating laboratories.

The choice of the food commodities was based on the following criteria;

(i) the commodities must be commonly grown and traded throughout the EU;
(ii) they must include at least one example of a fruit, a vegetable and a cereal crop as classified in the European Commission Directives on pesticide residues;
(iii) they should include examples of crops grown in the field, under protection and a stored commodity;
(iv) they must be easy to grow and to treat with pesticides, with the likelihood that measurable residues will ensue.

After due consideration of the above criteria, the following commodities were selected as typical examples;

Strawberries (soft fruit)
Spinach (green vegetable)
Carrots (root vegetable)
Tomatoes (protected crop)
Apples (tree fruit)
Wheat (stored cereal grain).

Production of samples containing incurred residues

To produce samples which contain 'naturally incurred' residues, crops need to be grown and treated under normal commercial conditions. Even then, some pesticides, such as many of the pyrethroids, are unlikely to give rise to measurable residues if they are applied according to 'good agricultural practice'. To maximise the possibility of producing residues approaching the Maximum Residue Levels (MRLs), as specified in the relevant EU Directive, the following steps may need to be taken: (1) Use maximum approved application rates; (2) use the maximum approved number of applications; (3) allow the minimum acceptable period between application and harvest; (4) apply the pesticide late in the growing season when crop growth rate is slowest; (5) blast freeze the crop samples immediately following harvest, and (6) cryogenically mill the crop to produce a homogeneous bulk sample.

Inter-laboratory comparison study

Twenty-four expert laboratories, including 22 from 12 EU member countries, and two from the Czech Republic, agreed to participate in this study which was broken down into four distinct phases over a four-year period; phase I is in progress at present.

Phase I was designed to test each laboratory's ability to measure residues of the 27 pesticides/metabolites by gas chromatography and identify any problems. Duplicate sets of six test solutions containing a combination of the 27 pesticides were prepared, tested for homogeneity and circulated to participating laboratories. Each participant was asked to analyse the six test solutions in triplicate on two separate occasions, at least 24 hours apart.

Phase II will involve the analysis of 'pesticide-free' and 'laboratory-spiked' samples of each commodity. This will test the methods in the presence of sample matrix.

Phases III and IV will involve the analysis of 'pesticide-free' and 'laboratory-spiked' samples as in Phase II, but will also include the samples prepared from agriculturally treated crops, i.e. samples containing 'incurred' residues.

These phases will fully test the relative performances of each method. The information will be passed on to

CEN which will allow them to publish the validation data in their Standard. This should not only lead to an increased confidence in pesticide residue data generated using these procedures, but also highlight their limitations and shortcomings.

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